
A New Method for Empirical Force Field Calculations on Localized and Delocalized Carbocations

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ABSTRACT

A new empirical force field method for localized and delocalized carbocations is described. Additional geometry parameters for carbocations were added to Allinger's MMP2 molecular mechanics program, which can treat delocalized π -systems. The effect of hyperconjugation in carbocations is introduced via a quantum chemical term into force field calculations for the first time. The calculated heats of formation are in excellent agreement with a wide range of experimental data; the largest deviations are about 3.5 kcal/mol. The calculated structures agree very well with those computed at correlated *ab initio* levels (MP2(full)/6-31G*). The relative energies and geometries of different conformations of representative carbocations also were in good agreement with MP4/6-31G*/MP2(full)/6-31G* results. © 1996 by John Wiley & Sons, Inc.

Introduction

Early in the development of empirical force field programs 30 years ago, carbocation problems, in particular bridgehead reactivity, motivated the extension of these methods to charged intermediates.¹ Bartlett and Knox were the first to recognize the inertness of bridgehead positions toward solvolysis reactions.² Bartlett suggested that the instability of the rigidly held, pyramidal

carbenium ion structures was responsible. In 1953 Doering et al. showed that the degree of distortion of sp^2 carbons out of planarity in bridgehead systems influences the reactivities.³ The reactivity differences in such S_N1 substitution reactions resulted from strain differences of carbocations and neutral precursor molecules. Therefore, Gleicher and Schleyer developed a force field program to calculate strain energies of bridgehead carbocations, like the 1-adamantyl and 1-norbornyl cations, and the corresponding neutral derivatives in 1967.¹ Later refinements of Mislow, Schleyer, and their co-workers led to the BIGSTRN program,⁴ which

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allowed the calculation of strain energies of carbocations. Müller and Mareda's parameterization of Allinger's MM2 program for localized tertiary carbocations improved and extended such strain energy treatments, especially for bridgehead systems.⁵ Reactivities ranging over 10^{20} could be correlated by the strain differences between cation and the neutral precursor.^{1,5,6}

However, all these methods were devised to relate strain energies with rate constants of solvolysis reactions rather than to compute heats of formation. In addition, possible changes in geometry due to alkyl group hyperconjugation in the carbocations were not included in the force field treatment. Indeed, no attempts to parametrize even π -delocalized carbocations, like allyl or benzyl, have been reported. The MMP2 method,⁷ which allows the calculation of delocalized neutral systems such as 1,3-butadiene, benzene, or naphthalene, provides the framework for the parameterization of delocalized carbocations. A further goal would be to obtain heats of formation for such systems.

For a long time, solvolysis reactivities and product distributions were the main data from which organic chemists drew conclusions about the nature of carbocations. Olah's discovery of conditions which allowed the direct experimental observation of carbocations by physical methods⁸ was a real breakthrough and permitted the general nature of many carbocations to be deduced reliably by the detailed interpretation of stable and dynamic nuclear magnetic resonance (NMR) spectra. However, only a limited number of X-ray structures of these unstable intermediates are available.⁹⁻¹² These agree well with computed geometries.¹³

High-level *ab initio* computations are the only general way at present to obtain detailed structures of carbocations (bond lengths, bond angles, etc.). However, the potential energy surfaces of carbocations are often extremely flat. So the different various theoretical levels often do not agree in the values for the critical geometrical parameters. Hence it is necessary to compare calculated with experimental results as far as this is possible. NMR chemical shifts and vibrational infrared (IR) spectra afford this opportunity.¹⁴

¹³C NMR chemical shifts of carbocations have long been known to be sensitive to changes of structure along the hyperconjugation-bridging continuum.¹⁵ Likewise the stretching frequencies of adjacent C-H groups also change considerably

and are a direct consequence of hyperconjugation.^{14,16}

Considerable experience with comparisons of experimental ¹³C NMR chemical shifts with those calculated by W. Kutzelnigg's IGLO program¹⁷ on MP2(full)/6-31G* optimized geometries often gave satisfying agreement; even better consistency of experimental and theoretical ¹³C chemical shifts were achieved by using J. Gauss's GIAO-MP2 method.¹⁸ Similar comparisons of experimental and computed IR spectra¹⁴ have shown that MP2(full)/6-31G* optimized geometries provide generally satisfactory carbocation structures. This method permits a large number of moderately large systems to be investigated at the same level.

Therefore, we calculated a large number of non-bridged carbenium ions at MP2(full)/6-31G* and used the geometries for the cation parameterization. The structures calculated by the force field method reproduce the *ab initio* geometries well. While the earlier cation force field parameterizations based on strain energies were not devised to reproduce carbocation structures,^{1,4,5} the aim of the present method is to reproduce *ab initio* geometries and hence to be able to predict the energies and geometries of larger carbocations.

Calculational Procedures

All *ab initio* optimizations used the GAUSSIAN 92¹⁹ program, the 6-31G* basis set,²⁰ and the second-order Møller-Plesset perturbation treatment (MP2(full)).²¹ Correlated *ab initio* methods are necessary for the optimization of cations, because restricted Hartree-Fock methods do not describe delocalization and resonance effects adequately.²² Semiempirical methods do not give satisfactory cation geometries and heats of formation. The single-point energies discussed in the text employ MP2(full)/6-31G* optimized geometries; for molecules up to six carbons, the fourth-order Møller-Plesset correction including single, double, triple, and quadruple excitations (MP4sdtq/6-31G*)²³ was applied, but only MP4sdq/6-31G*²³ for larger molecules. All optimized structures were characterized as minima by HF/6-31G* frequency calculations. Zero-point energy corrections were not customary for force field calculations, because their effect is included in the parameterization. The force field calculations were performed with the MM2(82) program,²⁴ which was adapted to a Convex C220.

Development of the New Method

Earlier force field programs parameterized for carbocations (see, e.g., ref. 4) used separate atom types for cationic C(sp²) atoms. This procedure is not necessary in our method. Instead, cationic carbons are treated as normal sp² carbons. The new parameters are added to the sp² carbons depending on the π -electron densities of these atoms, calculated by the self-consistent field (SCF) routine of MMP2, and their chemical environments. It is not necessary for the user to decide which C(sp²) atoms carry the positive charge.

BASIC CHANGES

We introduced a new variable to the input options, which indicates that a cation is to be computed and that one electron should be removed from the neutral π -system. Because delocalized carbenium ions, like the allyl or benzyl cations, always have an odd number of sp² carbons, the removal of one electron results in even numbers of π -electrons. Closed-shell π -systems are assumed.

It is important to compute resonance integrals of sp² carbons not bound to one another. These integrals are employed in MMP2, but the user must define the number of the integrals to be calculated and the designations of the nonbonded carbon atoms. Instead, we have introduced a new option for delocalized cations to define whether or not the nonbonded integrals should be computed. Hence it is very easy to estimate the magnitude of homoconjugation interactions in cations. The program determines the number of integrals and the designations of nonbonded carbons automatically.

For some larger systems, SCF convergence was difficult to achieve. These problems were overcome by introducing a damping factor in the force field SCF routine. Each element of the density matrix is calculated as a linear combination of old and new matrix elements:

$$Ed_{\text{new}}(i, j) = (1 - p) \cdot Ed_{\text{new}}(i, j) + p \cdot Ed_{\text{old}}(i, j) \quad (1)$$

where p is the damping factor and $Ed(i, j)$ is a density matrix element. By using a damping factor of 70%, SCF convergence could be achieved for almost all π -systems.

The electronic energy of a neutral system is calculated by eq. (2):

$$E_{\text{el}} = V_0 - \sum_{i=1}^{\text{norb}} W_i \quad (2)$$

where V_0 is the calculated SCF energy, W_i is the ionization potential of atom i , norb is the number of sp² carbons, and E_{el} is the real electronic π -energy.

By applying eq. (2) directly on carbocations, the electronic energy of the methyl cation is calculated as $-W_1 = 0.41014$ au (since V_0 [methyl cation] = 0 au). However, the electronic π -energy of the methyl cation should be set to 0 au. Consequently, a correction term of 0.41014 au (i.e., the absolute value of the ionization potential of an sp² carbon as defined in the MMP2 program independent of the charge) needs to be subtracted from the calculated energy to obtain the electronic π -energies of cations.

$$E_{\text{el}}(\text{cation}) = V_0 - \sum_{i=1}^{\text{norb}} W_i - 0.41014 \text{ au} \quad (3)$$

This correction sets the π -energy of methyl cation to be 0 kcal/mol.

SYSTEMS WITHOUT HYPERCONJUGATION

It is sufficient for the cation computations to remove one π -electron from the SCF calculations on neutral systems and to compute all nonbonded resonance integrals. This results in excellent π -electron densities as compared with MP2(full)/6-31G* (NBO analysis²⁵) values for all sp² carbons. The methyl cation is described as a system with one sp² carbon atom without any π -electrons. The π -electron densities of the allyl, the 1,3-pentadien-5-yl and the benzyl cations at MP2(full)/6-31G* agree well with the force field results. Table I lists π -electron densities of delocalized carbocations obtained by MP2(full)/6-31G* and MMP2 optimizations.

SYSTEMS WITH HYPERCONJUGATION

In alkyl cations, hyperconjugation (e.g., from methyl substituents) increases the electron density in the central p orbital. In contrast, a methyl group attached to an allyl or other π delocalized carbocation results in a decreased π -density of the attached carbon. This is due to the polarization of the electron density in the π -system away from the alkyl substituent. The 1-methylallyl cation demon-

TABLE I.
MMP2 and MP2(full) / 6-31G* π -Electron Densities
of Allyl, 1,3-Pentadien-5-yl Benzyl, 1-Methylallyl, and
 α -Methylbenzyl Cations.^a

Cation	Carbon atom	MP2(full)/6-31G*	MMP2
	1	0.441	0.473
	2	1.110	1.053
	1	0.612	0.603
	2	1.103	1.071
	3	0.557	0.574
	1	0.553	0.603
	2	1.115	1.090
	3	0.783	0.792
	4	1.034	1.019
	5	0.700	0.686
	1	0.438	0.367
	2	1.118	1.113
	3	0.518	0.521
	1	0.501	0.494
	2	1.134	1.155
	3	0.816	0.803
	4	1.023	1.016
	5	0.740	0.710
	6	1.030	1.017
	7	0.802	0.806

^aThe sums of the MP2(full) / 6-31G* π -electron densities of the allyl, 1,3-pentadien-5-yl and benzyl cations give numbers which are insignificantly lower than the numbers expected by resonance theory, due to a delocalization of electrons in Rydberg orbitals; the deviations of the sums of the π -electron densities of the 1-methylallyl and α -methylbenzyl cations from the values expected by resonance theory are discussed in the text.

strates this effect well (MP2(full)/6-31G* π -electron densities of the 1-methylallyl cation: C1: 0.438; C2: 1.118; C3: 0.518; c.f. Table I).

The effects of hyperconjugation could be parameterized by reducing the depth of the "potential hole" of the sp^2 carbon attached to the methyl group. The potential hole is a parameter that describes the ionization potential, W_i , of a C- sp^2 atom; according to Allinger's parameterization of the SCF routine, the potential hole has a fixed value (-11.16 eV). This procedure results in a shift of π -electrons to those carbons that have deeper potential holes and therefore to an increase of the positive charge at the carbon atom bound to the methyl group. Furthermore, the calculated electronic energy of the carbocations as a whole [eq. (3)] becomes more favorable. In this way, the reduction of the ionization potential, W_i , leads to a stabilization of the system.

For localized (e.g., alkyl) cations, eq. (3) reduces to eq. (4):

$$E_{el} = -W_1 - 0.41014 \text{ au} \quad (4)$$

Therefore, reduction of the ionization potential, W_1 , is equivalent to the electronic stabilization by hyperconjugation. The situation is more complicated in delocalized cations because the reduction of the ionization potential also influences the calculated SCF energy V_0 [c.f. eq. (3)]. However, the reduction of ionization potentials always leads to an electronic stabilization delocalized π -systems.

How should the ionization potential of an sp^2 carbon be changed? We used *ab initio* assessments of hyperconjugation energies to modify the ionization potentials. The assessment via NBO (natural bond orbital) analysis²⁵ employs Fukui's method²⁶ to calculate overlap energies E_{ij} of two orbitals i and j [eq. (5)]:

$$E_{ij} = \frac{f_{ij}^2}{\Delta \epsilon_{ij}} \quad (5)$$

where f_{ij} is the Fock matrix element of orbitals i and j , and $\Delta \epsilon_{ij}$ is the orbital energy difference of orbitals i and j .

The formula developed in detail in the following sections [eq. (13)] reproduces the E_{ij} values given by the Fukui method well. Hence, the ionization potentials, W_i , were changed by the values calculated by eq. (13). We examine in the next sections the various factors that influence the hyperconjugation energies in order to provide a mathematical description, which leads to the development of eq. (13).

Dependence on Dihedral Angles of Hyperconjugating Bonds

The magnitude of the hyperconjugation effect depends on the dihedral angle of the hyperconjugating bond with the plane of the sp^2 carbon and increases as this angle approaches 90° . The 2-propyl cation²⁷ illustrates this effect well (the results for the 2-propyl cation are listed in Table III). Therefore, the calculated hyperconjugation effect should depend on $(\sin(\omega_1) + \sin(\omega_2))/2$, where ω_1 and ω_2 are the dihedral angles of the hyperconjugating bond with two other atoms bound to the cationic center. This would favor conformations with one hyperconjugating bond perpendicular to the plane of the sp^2 carbon over conformations with one σ -bond parallel to this plane and, therefore, lead to large rotational barriers. However, *ab initio* calculations show that cations with rotating alkyl groups only have very low rotational barriers.^{27,28} We therefore assumed that hyperconjugation depends on the square of the sin of the dihe-

dral angles [eq. (6)]:

$$F \text{ hyp}(i, k, l) = k \cdot \left(\frac{\sin(\omega_1) + \sin(\omega_2)}{2} \right)^2 \quad (6)$$

where ω_1 and ω_2 are the dihedral angles of hyperconjugating bond with the plane of the sp^2 carbon atom, $F \text{ hyp}(i, k, l)$ is the hyperconjugation effect of bond $k-l$ with sp^2 carbon i , and k is a constant that involves all other effects which determine the strength of hyperconjugation interaction.

Equation (6) introduces the fact that the total hyperconjugative interaction energy of a methyl group does not depend on the dihedral angles of the hyperconjugating C-H bonds, since the total methyl group effect is not dependent on the individual dihedral angles [eq. (7)]:

$$k \cdot (\sin(\omega))^2 + k \cdot (\sin(\omega + 120^\circ))^2 + k \cdot (\sin(\omega - 120^\circ))^2 = \frac{3}{2} \cdot k \quad (7)$$

The complete hyperconjugation energy of a methyl group calculated by eq. (6) does not depend on the dihedral angle ω of a C-H bond and therefore on the conformation of the methyl group. Nevertheless, the effect of a single C-H bond depends on its dihedral angle with the two other atoms bound to the cationic center in a way that is analogous to the *ab initio* results. Therefore, the energy differences of various conformers of cations with C-H hyperconjugation effects are exclusively functions of steric energies, not of hyperconjugation energies.

Dependence on Orbital Energies of π -Orbitals and Hyperconjugating σ -Orbitals

Orbital interactions depend strongly on the energetic difference of their eigenvalues. The interaction is a maximum if the orbitals have the same eigenvalues and decreases with increasing energy difference. Fukui suggests a dependence of $1/\Delta \varepsilon_{ij}$ [c.f. eq. (5)]. However, the values calculated by Fukui's method become unrealistic with decreasing difference of the orbital eigenvalues. The calculated interaction energies are strongly overemphasized for orbitals with little energetic difference, and the calculation completely fails for orbitals with identical energy levels. We tried to avoid this

difficulty by introducing a different function:

$$F \text{ hyp}(i, k, l) = k \cdot \sum_{j=\text{nnumo}}^{\text{norb}} \exp(-c \cdot |\varepsilon_{\pi j} - \varepsilon_{\sigma}|) \quad (8)$$

where $\varepsilon_{\pi j}$ is the eigenvalue of the unoccupied π -orbital j , calculated by the SCF routine, ε_{σ} is the eigenvalue of hyperconjugating σ -orbital, c is a constant which describes the steepness of the weakening of the orbital interactions with increasing difference of orbital eigenvalues, nnumo is the number of the lowest unoccupied π -orbital, and norb is the number of sp^2 carbons and therefore the number of highest unoccupied π -orbital.

Equation (8) describes the interaction of the hyperconjugating σ -orbital with all unoccupied orbitals of the delocalized π -system. MMP2 computes reasonable eigenvalues for the π -orbitals of the cation; so we did not have to adjust these values. However, MMP2 does not calculate eigenvalues for σ -orbitals. We looked at a number of different cations with hyperconjugating methyl groups and found that the eigenvalues of the C-H bonds obtained by MP2(full)/6-31G* optimizations had almost the same magnitude. We therefore introduced the eigenvalue of the σ -orbital as a fixed parameter, depending simply on the kind of the hyperconjugating bond. Table IV shows the assumed eigenvalues for different kinds of hyperconjugating bonds.

MMP2 is not able to calculate eigenvalues of π^* -orbitals of localized cations, because localized cations have no occupied π -orbitals. We therefore introduced the eigenvalue of a singly unoccupied π -orbital as a fixed parameter. The situation is very simple for the methyl cation. The single value of the one-dimensional Fock matrix is the ionization potential of the sp^2 carbon, and therefore the eigenvalue has to be identical with it. Hyperconjugation leads to a shift toward more positive quantities. By comparison with *ab initio* results for the methyl, ethyl, 2-propyl, and *t*-butyl cations (MP2(full)/6-31G* optimizations), we found suitable values for primary, secondary, and tertiary cations and introduced them to MMP2 as fixed parameters. Table IV shows the assumed eigenvalues for the π^* -orbitals of primary, secondary, and tertiary cations.

Dependence on MO Coefficients of π^* -Orbitals

According to eq. (5), the hyperconjugation energy depends on the square of the Fock matrix

element between donor σ -orbital and acceptor π^* -orbital. We consistently assumed that hyperconjugation depends on the square of the π^* -orbital coefficients. This relation is described by eq. (9):

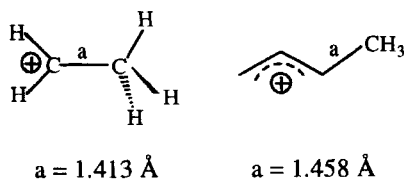
$$F \text{ hyp}(i, k, l) = k \cdot \sum_{j=\text{nlorb}}^{\text{norb}} v_{ij}^2 \quad (9)$$

where v_{ij} is the orbital coefficient of orbital j on atom i .

Equation (9) assumes that the contribution of the hyperconjugating σ -orbital to the Fock matrix element is constant for a constant dihedral angle of the hyperconjugating σ -orbital toward the plane of the sp^2 carbon and for some constant geometry parameters, which will be mentioned later. The validity of this approximation is confirmed by NBO analysis for a number of classical carbocations (ethyl cation, 2-propyl cation, *t*-butyl cation, 1-methylallyl cation, and α -methylbenzyl cation). Nevertheless, the contribution of the hyperconjugating σ -orbital depends on the kind of the σ -orbital. The contribution of a hyperconjugating $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ orbital to the Fock matrix element is larger than the contribution of a hyperconjugating $\text{C}(\text{sp}^3)\text{--H}$ orbital. This effect can be regarded by introducing different overlap integrals for the different kinds of hyperconjugating σ -bonds (c.f. the section titled "Summary of the Effects").

Dependence on the $\text{C}\text{--}\text{sp}^3\text{--C}^+$ Bond Length

All structures of cations with hyperconjugating alkyl groups show a significant shortening of the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bond due to a better overlap of the hyperconjugating $\text{C}\text{--H}$ σ -orbital with the unoccupied π^* -orbitals of the cationic center. The shortening increases with increasing strength of hyperconjugation. On the other hand, the shortening of this bond itself leads to a stronger hyperconjugation interaction. This effect can be shown clearly by comparing the classical ethyl and 1-methylallyl cations.



The stronger hyperconjugation effect of the ethyl cation leads to a shortening of the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bond, but the shorter bond itself causes a stronger

hyperconjugation effect. We examined this effect by doing single-point SCF calculations on the classical ethyl cation and 1-methylallyl cation for a number of different $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bond lengths and looked at the different $\sigma\text{--}\pi^*$ overlap energies, which were calculated in NBO analysis by Fukui's method. The question on the real structure of the ethyl cation is not of interest for these theoretical investigations. Table II and Figure I give the results.

The results prove that hyperconjugation depends linearly on the decreasing bond length in the range from 1.41 \AA to 1.51 \AA . For smaller and larger bond lengths the dependence is not linear, but these ranges are not of interest. The straight lines intersect the x -axis at 1.72 \AA for both cations. A similar behavior has been found for all cations that were examined. The error made if a linear dependence is assumed is maximal for the ethyl cation, and even in this case it is less than 0.50 kcal/mol. Consistently, the dependence of hyperconjugation energy on the bond length of a $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bond can be described by eq. (10):

$$F \text{ hyp}(i, k, l) = k \cdot (1.72 - r_{ik}) \quad (10)$$

where r_{ik} is the bond length of cationic sp^2 carbon atom to the sp^3 carbon atom attached to it.

Dependence on the $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)\text{--C}^+$ and $\text{H}\text{--C}(\text{sp}^3)\text{--C}^+$ Angles

Analogous to eq. (10), a similar correlation can be found for the dependence of hyperconjugation on the angle of the sp^2 carbon with the hyperconjugating bond. Table III shows some of these angles for cations with strong hyperconjugation effects from MP2(full)/6-31G* optimizations. It can be seen that the proposed angle diminishes with increasing strength of hyperconjugation to achieve a better $\sigma\text{--}\pi^*$ overlap. Increasing the strength of hyperconjugation leads to an increasing deviation of this angle from the tetrahedral value of 109.5°. Table III lists typical examples that show geometry parameters, which determine the strength of hyperconjugation interactions.

We found that it was not necessary to describe this effect by adding a new item. A slight modification of eq. (10) was able to simulate this effect simply. We calculate the coordinates of a fictive point positioned on the hyperconjugating bond, which divides this bond in a ratio of 1:4. Subse-

TABLE II.

Dependence of the Strength of a σ - π^* Overlap of a C-H Bond in the Classical Ethyl and 1-Methylallyl Cations on the C(sp²)-C(sp³) Bond Length r .

$r/\text{\AA}$	1.33	1.35	1.37	1.39	1.41	1.43
Hyperconjugation energy of ethyl cation / kcal / mol	35.24	32.73	30.39	28.19	26.12	24.19
Hyperconjugation energy of 1-methylallyl cation / kcal / mol	23.83	21.96	20.22	18.62	17.13	15.76
$r/\text{\AA}$	1.45	1.47	1.49	1.51	1.53	1.55
Hyperconjugation energy of ethyl cation / kcal / mol	22.38	20.68	19.09	17.61	16.23	14.94
Hyperconjugation energy of 1-methylallyl cation / kcal / mol	14.50	13.34	12.26	11.27	10.35	9.51

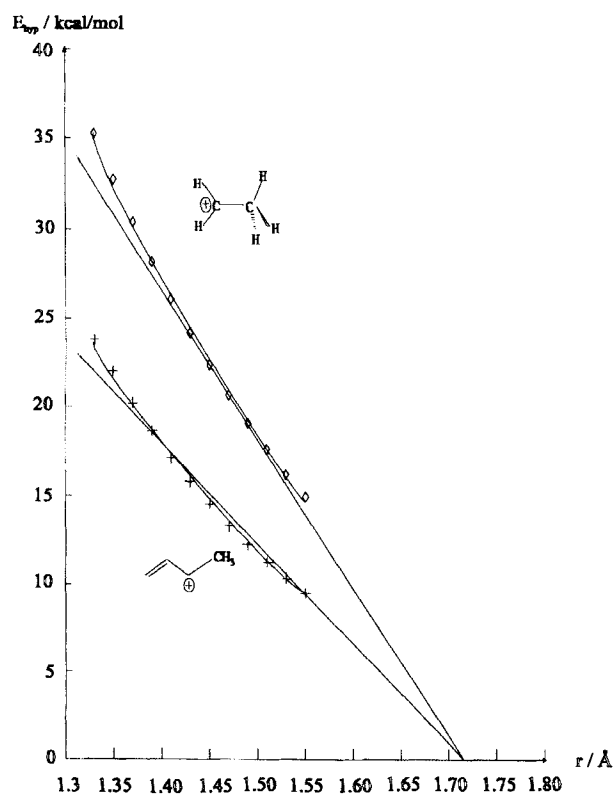


FIGURE 1. Dependence of the hyperconjugation energy E_{hyp} on the bond length r of the C(sp²)-C(sp³) Bond.

TABLE III.

Examples for Geometric Parameters that Determine the Strengths of Hyperconjugation Interactions.

C-sp ² -C-sp ³ Bond lengths of primary, secondary and tertiary cations (MP2(full)/6-31G* results)		Bond angles of the cationic center with the hyperconjugating bond (MP2(full)/6-31G* results)	
Cation	C-sp ² -C-sp ³ bond length / Å	Cation	Angle
	1.414		C1-C2-H3: 107.1°
	1.438		C1-C2-C3: 98.3°
	1.459		C1-C2-H3: 108.7°
			C1-C2-C3: 105.9°
σ - π^* Orbital interaction-dependence on the dihedral angles of the hyperconjugating bond with the plane of the cationic center in the 2-propyl cation			
	Dihedral angle:		σ - π^* Interactions calculated by Fukui's method (kcal/mol)
	H1-C2-C3-H4: 76.9°		38.1
	H1-C2-C3-H5: -33.7°		6.2
	H1-C2-C3-H6: -167.2°		1.2

quently, we calculate the distance of this point to the cationic center r_l . Then we compute the radius-dependent contribution of hyperconjugation by eq. (11), which is a modification of eq. (10):

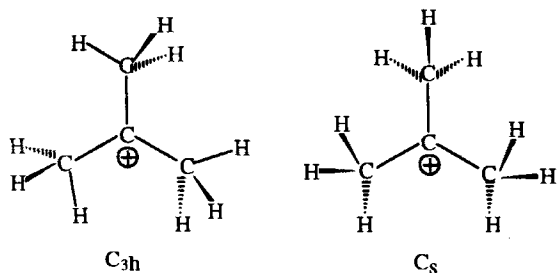
$$F_{\text{hyp}}(i, k, l) = k \cdot (r_{cc} - r_l) \quad (11)$$

$$r_{cc} = \begin{cases} 1.822 & \text{for C(sp}^2\text{)}\text{--H hyperconjugation} \\ 2.140 & \text{for C(sp}^3\text{)}\text{--C(sp}^3\text{)} \text{ hyperconjugation} \\ 2.005 & \text{for C(sp}^2\text{)}\text{--H hyperconjugation} \\ 2.030 & \text{for C(sp}^2\text{)}\text{--C(sp}^2\text{)} \text{ hyperconjugation} \end{cases}$$

$$r_l = \sqrt{(x_i - x_l)^2 + (y_i - y_l)^2 + (z_i - z_l)^2}$$

where x_i , y_i , and z_i are the coordinates of a cationic sp^2 carbon atom, and x_l , y_l , and z_l are the coordinates of the fictive point.

The variable r_l of eq. (11) diminishes with decreasing angle of the hyperconjugating bond with the sp^2 carbon, and therefore the factor $F_{\text{hyp}}(i, k, l)$, which describes the strength of hyperconjugation interaction of bond $k\text{--}l$ with the cationic center i , increases with decreasing angle. In this way eq. (11) describes the angle dependence of hyperconjugation well. It is important to choose the correct coordinates of the fictive point. The distance of this point to atom k is 20% of the length of the hyperconjugating bond. An enlargement of this distance would induce a reinforcement of the angle dependence of hyperconjugation, and therefore conformers which have one very strong hyperconjugating bond and a very small angle of this bond with the cationic center would be favored too much over conformers, which have no outstanding strong hyperconjugation interaction. A reduction of this distance would lead to the reverse effect.



We used the *t*-butyl cation to find the correct coordinates of the fictive point. According to MP2(full)/6-31G* optimizations,²⁸ structures with C_s symmetry and C_{3h} symmetry are minima in the C_4H_9^+ energy surface with a very low energy

difference of 0.08 kcal/mol in favor of the C_s structure. This system is very sensitive to the discussed effect because the C_s structure presents three strong hyperconjugation interactions, while the C_{3h} structure shows only weaker hyperconjugative effects. We were thus able to adjust the correct coordinates for the fictive point by comparing the force field results for both conformers for a number of different coordinates of this point.

Equation (11) includes the fact that hyperconjugating $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ bonds show a larger angle dependence than C--H bonds, because the distance of the fictive point to atom k is larger for $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ bonds than for C--H bonds (larger bond length of the hyperconjugating bond). This effect can be verified very easily by comparing the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ angle in the 1-adamantyl and 1-ethylallyl cations with the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)\text{--H}$ angle in the classical ethyl and 1-methylallyl cations (c.f. Table III).

Finally, we had to consider that the 1.72 Å constant of eq. (10) had to be changed, because the distance r_l of eq. (11) is larger than 1.72 Å and the result obtained by eq. (11) would be negative. Therefore, we determined the distance of the fictive point from the cationic center, when the central bond $i\text{--}k$ has a bond length of 1.72 Å. The computed values for the different kinds of hyperconjugating bonds accompany eq. (11).

Summary of the Effects that Determine the Strength of Hyperconjugation Interactions

The effects that determine the strength of hyperconjugation interactions can be combined into a single equation:

$$F_{\text{hyp}}(i, k, l) = I \cdot (\sin(\omega))^2 \cdot \sum_{j=\text{nlumo}}^{\text{norb}} [v_{ij}^2 \cdot \exp(-c) \cdot |\epsilon_{\pi j} - \epsilon_{\sigma}|] \cdot (r_{cc} - r_l) \quad (12)$$

The term $I = \int \Phi_{\sigma} \Phi_{\pi}^* d\tau$ is an overlap integral of a σ -MO with a π^* -MO for standard conditions (i.e., the bond length $i\text{--}k$ is 1.0 Å; the angle $i\text{--}k\text{--}l$ is 109.5°; the dihedral angle of bond $k\text{--}l$ with plane of atom i is 90°; the orbital coefficient of π^* -orbital is 1.0; and the two orbitals have the same eigenvalues); it is a fixed value which depends on the kind of the hyperconjugating bond. The values assumed are listed in Table IV.

TABLE IV.
Assumed Parameters for Different Variables that Determine the Strength of Hyperconjugation Interactions According to Eqs. (12) and (13).

Assumed Eigenvalues for Hyperconjugating σ -Bonds		Assumed Overlap Integrals for a σ - π^* Overlap for Different Kinds of Hyperconjugating σ -Bonds	
Hyperconjugating Bond	Eigenvalue / au	Hyperconjugating Bond	Overlap Integral / au
C(sp ³)–H	–0.89	C(sp ³)–H	0.27233
C(sp ³)–C(sp ³)	–0.94	C(sp ³)–C(sp ³)	0.17494
C(sp ²)–H	–1.24	C(sp ²)–H	0.13635
C(sp ²)–C(sp ²)	–0.91	C(sp ²)–C(sp ²)	0.31790
Assumed Eigenvalues for Unoccupied π^* -Orbitals of Localized Cations		Assumed Repulsion Integrals for a σ - π Repulsion for Different Kinds of Hyperconjugating σ -Bonds	
Cation	Eigenvalue / au	Bond	Repulsion Integral / au
Methyl cation	–0.410	C(sp ³)–H	–0.1584
Primary cation	–0.388	C(sp ³)–C(sp ³)	–0.3098
Secondary cation	–0.367	C(sp ²)–H	–0.0718
Tertiary cation	–0.356	C(sp ²)–C(sp ²)	–0.1819

Table V shows some values for the strength of hyperconjugation computed by eq. (12) and compares them with the results obtained by Fukui's method (MP2(full)/6-31G* optimized geometries). It can be seen that the values for very strong hyperconjugation effects, which are overestimated by Fukui's method, are computed to be weaker by eq. (12). This is due to the weaker increase of the hyperconjugation interaction with decreasing difference of the orbital eigenvalues, described by eq. (8). On the other hand, the values for weak hyperconjugation interactions are overestimated by eq. (12) (maximal difference that could be found less than 4.0 kcal/mol). This failure of eq. (12) seems to be less serious because of the small contributions of weak hyperconjugation interactions to the complete effect of an alkyl group. The values calculated for intermediate hyperconjugation interactions by Fukui's method are reproduced by eq. (12) well.

For delocalized cations, the hyperconjugating σ -orbitals not only interact with π^* -orbitals, but these orbitals show repulsive interactions with occupied π -orbitals of the delocalized π -system, too. Therefore, the values calculated by eq. (12) are modified by a correction value for repulsive interactions. The correction formula has been developed analogously to eq. (12), and the final values

for hyperconjugation interactions are computed by eq. (13):

$$F \text{ hyp}(i, k, l) = F \text{ hyp}(i, k, l) + R \cdot (\sin(\omega))^2 \cdot \sum_{j=1}^{\text{n homo}} [v_{ij}^2 \cdot \exp(-c) \cdot |\epsilon_{\pi_j} - \epsilon_{\sigma}|] \cdot \frac{1}{r_m} \quad (13)$$

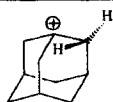
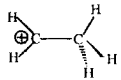
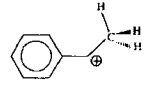
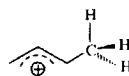
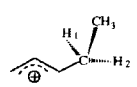
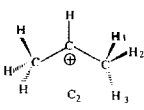
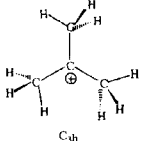
The term $R = \int \Phi_{\sigma}(1/r) \Phi_{\pi} d\tau$ is a repulsion integral of a σ -MO and a π -MO for standard conditions [c.f. integral I in eq. (12)]; it is a fixed value which depends on the kind of the hyperconjugating bond. The assumed values are listed in Table IV. The term r_m is the distance of cationic center i to the center of hyperconjugating bond k – l , and n homo is the number of highest occupied π -orbital.

Finally, the depths of the ionization potentials of the sp² carbons are changed by the estimated values for hyperconjugation interaction.

$$W_i = W_i + \sum_{k,l} F \text{ hyp}(i, k, l) \quad (14)$$

Application of eq. (14) results in the calculation of reasonable electron densities for alkyl-substituted delocalized cations. Illustrative examples are the

TABLE V.
Energies of Hyperconjugative Interactions Calculated
by Fukui's Method (MP2(full) / 6-31G* Optimized
Structures ($E_{\sigma-\pi^*}$) and by Eq. (12) (E_{hyp}).

Cation	Hyperconjugating bond	E_{hyp} / kcal/mol	$E_{\sigma-\pi^*}$ / kcal/mol
	C-sp ³ -C-sp ³	30.33	38.25
	C-sp ³ -H	4.71	1.64
	C-sp ³ -H	22.48	25.98
	C-sp ³ -H	10.20	9.86
	C-sp ³ -H	12.61	14.03
	C-sp ³ -C-sp ³	17.86	19.43
	C-sp ³ -H1	9.14	6.54
	C-sp ³ -H2	0.92	0.64
	C-sp ³ -H1	6.38	6.22
	C-sp ³ -H2	4.89	1.21
	C-sp ³ -H3	28.38	38.16
	C-sp ³ -H	18.07	16.37

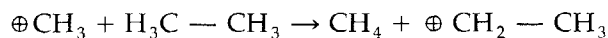
1-methylallyl and α -methylbenzyl cations. Table I shows the electron densities for these molecules, obtained by MP2(full)/6-31G* optimizations, and compares them with the electron densities computed by MMP2.

The π -electron densities on carbon atoms 2 and 3 of the 1-methylallyl cation, computed by the two different methods, agree well. The π -electron density of atom 1 is found to be significantly lower by MMP2 than by *ab initio* methods. This deviance is a consequence of the electron donor effect of the hyperconjugating bonds, which increases the π -electron density of the alkylated carbon atom (sum of π -electrons at MP2(full)/6-31G*: 2.074). This electron donor effect cannot be reproduced by MMP2, since MMP2 does not include σ -electrons (sum of π -electrons: 2.00). Nevertheless, the correspondence of π -electron densities on atoms 2 and 3

shows that the shift of π -electrons from atom 1 to atoms 2 and 3 is described correctly by MMP2. For the α -methylbenzyl cation, the electron densities calculated by the two different methods correspond very well for all carbon atoms. This agreement is a result of the weak electron donor effect of the methyl group (sum of the π -electrons at MP2(full)/6-31G*: 6.046) in this system.

REPULSIVE FORCES

The stabilization effect of the methyl group in the classical ethyl cation can be computed by an isodesmic equation:



We used the C_s structure of the classical ethyl cation for the computation of this isodesmic equation, although the classical ethyl cation is not a minimum on the MP2(full)/6-31G* energy hypersurface of the C₂H₅⁺ cation, because the real structure of this cation is not important for the question of hyperconjugative stabilization of alkyl groups in hypothetical classical cations. This stabilization effect is found to be 34.8 kcal/mol at MP4sdtq/6-31G*//MP2(full)/6-31G*, which is in contrast to the value estimated by the NBO method for the overlap of the C-H— σ bonds with the π^* -orbital. These NBO values suggest a stabilization of 52.0 kcal/mol (c.f. Table V). This contradiction can be resolved by assuming that the shortening of the C(sp²)—C(sp³) bond not only leads to a reinforcement of the hyperconjugative stabilization, but also to a reinforcement of the core-core repulsion of the two carbon atoms and the approaching hydrogen atoms. The reduction of the carbon-carbon distance is treated by the assumption of a 1/*r*-dependent force, which is described by eq. (15):

$$E_{\text{rep}}(i, k) = c \cdot \left(\frac{1}{r} - \frac{1}{1.497} \right) \quad (15)$$

where *i* is the cationic sp² carbon atom, *k* is the sp³ carbon attached to atom *i*, $E_{\text{rep}}(i, k)$ is the repulsive energy of atoms *i* and *k*, and *r* is the distance of atoms *i* and *k*.

The MMP2 bond parameter for a C(sp²)—C(sp³) bond is 1.497 Å, and therefore eq. (15) calculates the repulsive energy that results from the shortening of a bond, which has a natural bond length of 1.497 Å. The constant *c* is adjusted so

TABLE VI.
Torsional Constants for Carbocations and Conditions that Determine their Assignment.

Angle Type	V1	V2	V3	Conditions that Determine the Assignment of the Torsional Constants
C(sp ²)–C(sp ²)–C(sp ²)–C(sp ²)	–1.55	—	0.50	All C(sp ²) atoms carry a positive charge
	–1.40	—	0.50	Only second and third C(sp ²) atoms carry a positive charge
	2.00	—	0.50	Only first and fourth C(sp ²) atoms carry a positive charge
	–0.89	—	0.50	Second or third C(sp ²) atoms carry a positive charge
C(sp ²)–C(sp ²)–C(sp ²)–H	1.55	—	–1.70	Second or third atom is a tertiary C(sp ²) atom
	0.63	—	–1.70	All other cations
H–C(sp ²)–C(sp ²)–H	2.15	—	0.75	One carbon atom terminates a carbon chain
	0.95	—	–0.75	All other cations
C(sp ³)–C(sp ³)–C(sp ²)–H	–2.45	5.35	–3.55	Localized primary cations
	1.90	–0.55	3.25	Localized secondary cyclic cations
	5.75	9.35	–3.55	Localized secondary acyclic cations
	–2.45	–0.55	1.75	All other cations
H–C(sp ³)–C(sp ²)–H	1.10	0.75	0.40	C(sp ²) atom is attached to a tertiary C(sp ²) atom
	–0.60	0.50	–0.38	All other cations
H–C(sp ³)–C(sp ²)–C(sp ³)	–0.50	0.60	–0.27	C(sp ²) atom is attached to a tertiary C(sp ²) atom
	–1.85	0.60	–0.47	All other cations
H–C(sp ³)–C(sp ²)–C(sp ²)	–1.35	0.00	–0.545	C(sp ²) atom attached to the C(sp ³) atom carries a positive charge
	–0.30	0.00	–0.40	C(sp ²) atom attached to the C(sp ³) atom does not carry a positive charge
C(sp ²)–C(sp ³)–C(sp ²)–C(sp ²)	–0.75	1.05	0.35	—
C(sp ²)–C(sp ²)–C(sp ²)–C(sp ³)	–2.10	—	2.70	C(sp ³) atom is attached to at least two C(sp ²) atoms
	1.45	—	–0.55	C(sp ²) atom attached to the C(sp ³) atom terminates a chain of C(sp ²) atoms
	–1.60	—	0.90	All other cations
C(sp ²)–C(sp ²)–C(sp ³)–C(sp ³)	–4.45	2.55	–0.70	C(sp ³) atom bound to the C(sp ²) atom is attached to at least two C(sp ³) atoms (<i>i</i> -propyl, <i>t</i> -butyl groups)
	–5.22	2.95	1.45	Second C(sp ³) atom is attached to at least two C(sp ³) atoms (e.g., <i>n</i> -propyl groups)
	–4.82	1.98	1.62	All other cations
C(sp ³)–C(sp ²)–C(sp ²)–C(sp ³)	–0.10	—	0.60	One C(sp ²) atom carries a positive charge and at least one of the two C(sp ²) atoms is attached to a hydrogen atom

TABLE VI.
(continued)

Angle Type	V1	V2	V3	Conditions that Determine the Assignment of the Torsional Constants
	-0.10	—	-3.30	One C(sp ²) atom carries a positive charge and none of the two C(sp ²) atoms is attached to a hydrogen atom
	-0.10	—	0.85	All C(sp ²) atoms carry a positive charge
	-0.10	—	2.80	No C(sp ²) atom carries a positive charge, but at least one of these atoms is attached to a C(sp ²) atom, which carries a positive charge
C(sp ³)–C(sp ²)–C(sp ³)–C(sp ²)	3.25	-3.25	0.95	—
C(sp ³)–C(sp ³)–C(sp ²)–C(sp ³)	1.80	-2.60	4.35	Localized cations
	1.50	-5.00	0.50	Delocalized cations
H–C(sp ²)–C(sp ³)–C(sp ²)	0.00	3.20	1.15	—
C(sp ³)–C(sp ²)–C(sp ²)–H	0.65	—	-0.55	C(sp ²) atom attached to the hydrogen atom terminates a row of C(sp ²) atoms
	-0.65	—	-0.30	All other cations
C(sp ²)–C(sp ³)–C(sp ³)–C(sp ³)	-1.45	0.75	-0.95	C(sp ²) atom carries a positive charge
C(sp ²)–C(sp ³)–C(sp ³)–H	0.75	-0.50	-0.40	C(sp ²) atom carries a positive charge
C(sp ³)–C(sp ³)–C(sp ³)–C(sp ³)	-1.25	-0.45	-2.32	One C(sp ³) atom is attached to a C(sp ²) atom, which carries a positive charge

V1: Onefold torsional constant; V2: twofold torsional constant; V3: threefold torsional constant; primary C(sp²) atom: C(sp²) atom that is connected to one C(sp²) atom; secondary C(sp²) atom: C(sp²) atom that is connected to two C(sp²) atoms; tertiary C(sp²) atom: C(sp²) atom that is connected to three C(sp²) atoms.

that the absolute values of the derivatives of this repulsion energy are adapted to the absolute values of the derivatives of the attractive hyperconjugation energy at the calculated equilibrium bond lengths for each cation:

$$\left| \left(\frac{\partial E_{\text{rep}}}{\partial r} \right)_{r=r_0} \right| = \left| \left(\frac{\partial E_{\text{hyp}}}{\partial r} \right)_{r=r_0} \right| \quad (16)$$

where r_0 is the equilibrium bond length of a C⁺–C(sp³) bond.

The rising core–core repulsion of the hydrogen atoms as they approach is treated in a different way. It is almost impossible to find a simple equation similar to eq. (15) which is consistent with eq. (16). Therefore, we established an increment system that depends on the number of hydrogen atoms attached to the cationic center, the number of hyperconjugating hydrogen atoms, the number of C(sp³) atoms attached to the C(sp²) atom, and the number of hyperconjugating C(sp³) atoms, and we added a fixed energy, which was calculated according to this increment system to the computed repulsion energy [eq. (17)]:

$$E_{\text{rep}}(i, k) = E_{\text{rep}}(i, k) + \begin{cases} 0.0060 \cdot \text{NHH} + 0.0185 \cdot \text{NSS} + 0.0075 \cdot (\text{NCC} - \text{NSS}) & \text{for primary cations} \\ 0.00296 \cdot \text{NHH} + 0.00495 \cdot \text{NSS} + 0.0034 \cdot (\text{NCC} - \text{NSS}) & \text{for secondary cations} \\ 0.00225 \cdot \text{NHH} + 0.002993 \cdot \text{NSS} + 0.0034 \cdot (\text{NCC} - \text{NSS}) & \text{for tertiary cations} \end{cases} \quad (17)$$

where $E_{\text{rep}}(i, k)$ is calculated in atomic units, NHH is the number of hyperconjugating hydrogen atoms, NSS is the number of sp^3 carbons which are bound to the cationic center and to at least one hyperconjugating sp^3 carbon, NCC is the number of hyperconjugating sp^3 carbons, and $k \cdot (\text{NCC} - \text{NSS})$ is a correction increment for *i*-propyl- and *t*-butyl groups. Subsequently, the energy calculated by eq. (17) is added to the computed σ -energy of the π -system:

$$E_{\sigma} = E_{\sigma} + \sum_{i, k} E_{\text{rep}}(i, k) \quad (18)$$

Different increments for primary, secondary, and tertiary cations allow us to introduce the fact that primary, secondary, and tertiary cations have different $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bond lengths and therefore different hyperconjugation interactions, although single-point SCF calculations showed that hyperconjugation interactions have the same magnitude for primary, secondary, and tertiary cations with corresponding bond lengths and dihedral angles.

GEOMETRY PARAMETERS

Bond Parameters

Bond length and force constant parameters are adjusted according to the data obtained by eq. (12) and eq. (17). The parameters for a hyperconjugating bond *k*–*l* attached to a cationic center *i* are corrected according to eq. (19) and eq. (20) due to an elongation of this bond as a result of hyperconjugation:

$$l_0(k, l) = 1.523 + 1.22 \cdot F \text{ hyp}(i, k, l) \quad (19)$$

$$K(k, l) = 4.40 - 16.0 \cdot F \text{ hyp}(i, k, l) \quad (20)$$

where l_0 is the bond length parameter and *K* is the parameter for the bond constant.

The parameters for a hyperconjugating $\text{C}(\text{sp}^3)\text{--H}$ bond are treated similarly:

$$l_0(k, l) = 1.113 + 0.55 \cdot F \text{ hyp}(i, k, l) \quad (21)$$

$$K(k, l) = 4.60 - 12.0 \cdot F \text{ hyp}(i, k, l) \quad (22)$$

The bond lengths of $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bonds *i*–*k* are shortened depending on the strength of hyperconjugation interactions. We considered this effect by

a correction of bond parameters.

$$l_0(i, k) = 1.497 - 0.351 \cdot \sum_1 F \text{ hyp}(i, k, l) + 1.7 \cdot E_{\text{rep}}(i, k) \quad (23)$$

$$K(i, k) = 4.40 + 25.0 \cdot \sum_1 F \text{ hyp}(i, k, l) \quad (24)$$

The bond parameters for $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ bonds of neutral molecules are changed according to the bond orders computed by the SCF calculation. We found that this assumption works well for delocalized cations. The only exceptions have been found for bonds of two $\text{C}(\text{sp}^2)$ atoms carrying a positive charge. These bonds proved to be longer than calculated using the foregoing assumption because of the charge–charge repulsion. We found it necessary to correct the parameters by the sum of the charges:

$$l_0 = l_0 + 0.13 \cdot (q_i + q_k)^2 \quad (25)$$

where q_i is the positive charge of $\text{C}(\text{sp}^2)$ atom *i*: $q_i = 1. - \text{Ed}(i, i)$, q_k is the positive charge of $\text{C}(\text{sp}^2)$ atom *k*: $q_k = 1. - \text{Ed}(k, k)$, and *Ed* is the density matrix element.

Angle Parameters

The angle parameters are changed depending on the results of the SCF calculation analogous to the procedure with bond parameters.

1. *Angle type* $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)\text{--C}(\text{sp}^2)$. The parameters for this angle type have to be varied due to the overlap of the π -orbitals of the two marginal $\text{C}(\text{sp}^2)$ atoms (homoconjugation effects):

$$\text{Ang}(i, k, l) = 122. - 4.2 \cdot \text{Ed}(i, l) \quad (26)$$

$$K(i, k, l) = 0.31 + 0.2 \cdot \text{Ed}(i, l) \quad (27)$$

where *Ed*(*i*, *l*) is the density matrix element of the two marginal $\text{C}(\text{sp}^2)$ atoms, *Ang*(*i*, *k*, *l*) is the bending parameter of the angle *i*–*k*–*l*, and *K*(*i*, *k*, *l*) is the bending constant of the angle *i*–*k*–*l*. The out-of-plane bending constant is changed according to the charge of the central carbon atom:

$$\text{Sopb}(i, k, l) = 0.05 + 0.9 \cdot (1. - \text{Ed}(k, k)) \quad (28)$$

where *Sopb*(*i*, *k*, *l*) is the out-of-plane bending constant of a sp^2 carbon *k*.

2. Angle type $H-C(sp^2)-H$. The bending constant of this angle type is enlarged depending on the charge of the central carbon atom.

$$K(i, k, l) = 0.320 + 4.2 \cdot (1. - Ed(k, k)) \quad (29)$$

3. Angle type $C(sp^3)-C(sp^2)-C(sp^3)$. The parameters of this angle type are varied analogously to eq. (29).

$$Ang(i, k, l) = 117.2 - 2 \cdot (1. - Ed(k, k)) \quad (30)$$

$$K(i, k, l) = 0.45 + 0.6 \cdot (1. - Ed(k, k)) \quad (31)$$

The out-of-plane bending constant is enlarged depending on the sum of the hyperconjugation interactions, because we felt that the rigidity of the carbon skeleton against out-of-plane bending is determined by the $\sigma-\pi^*$ overlap.

$$Sopb(i, k, l) = 0.05 + 8.0 \cdot \sum_{m, n} F \text{ hyp}(k, m, n) \quad (32)$$

4. Angle type $C(sp^3)-C(sp^2)-H$. This angle type is treated similar to angle type $H-C(sp^2)-H$.

$$K(i, k, l) = 0.45 + 0.90 \cdot (1. - Ed(k, k)) \quad (33)$$

$$Sopb(i, k, l) = 0.05 + 2.2 \cdot (1. - Ed(k, k)) \quad (34)$$

5. Angle type $C(sp^2)-C(sp^2)-H$. The bending parameters for this angle type are changed according to the charge of the central carbon atom, too.

$$Ang(i, k, l) = 122. - 0.5 \cdot (1. - Ed(k, k)) \quad (35)$$

$$K(i, k, l) = 0.36 + 0.2 \cdot (1. - Ed(k, k)) \quad (36)$$

$$Sopb(i, k, l) = 0.05 + 1.0 \cdot (1. - Ed(k, k)) \quad (37)$$

6. Angle type $C(sp^2)-C(sp^2)-C(sp^3)$. The parameters for this angle type are varied analogously to eqs. (35), (36), and (37).

$$Ang(i, k, l) = 122. + 7.0 \cdot (1. - Ed(k, k)) \quad (38)$$

$$K(i, k, l) = 0.55 - 0.9 \cdot (1. - Ed(k, k)) \quad (39)$$

$$Sopb(i, k, l) = 0.05 + 1.0 \cdot (1. - Ed(k, k)) \quad (40)$$

7. Angle type $C(sp^2)-C(sp^3)-C(sp^2)$. The problem with this angle type is the large range of the calculated angles (MP2(full)/6-31G* results) depending on the homoconjugation of the two marginal sp^2 carbons. Therefore, we developed formulas that depend on the density matrix element of the homoconjugating sp^2 carbons as well

as the difference of this charges.

$$Ang(i, k, l) = 109.47 - 80.4 \cdot Ed(i, l) \cdot (1. - Pldif)^2 + 12.5 \cdot Pldif \quad (41)$$

$$K(i, k, l) = 0.45 + 0.5 \cdot Ed(i, l) \cdot (1. - Pldif)^2 - 0.3 \cdot Pldif \quad (42)$$

$$Pldif = |Ed(i, i) - Ed(l, l)|$$

The correct application of eqs. (41) and (42) enables the calculation of structures with strong homoconjugation, like the homotropylium²⁹ or 7-norbornenyl cations, as well as the calculation of structures with small homoconjugation effects.

8. Angle type $C(sp^2)-C(sp^3)-C(sp^3)$. The angles deviate from tetrahedral angle because of hyperconjugation effects and are calculated to be smaller the larger the hyperconjugation effect is (c.f. Table III). We developed eqs. (43) and (44) to describe this effect realistically.

$$Ang(i, k, l) = 110. - 2700 \cdot F \text{ hyp}^2(i, k, l) \quad (43)$$

$$K(i, k, l) = 0.36 + 400 \cdot F \text{ hyp}^2(i, k, l) \quad (44)$$

In connection with eq. (11), eqs. (43) and (44) allow a good description of the angle dependence of hyperconjugation.

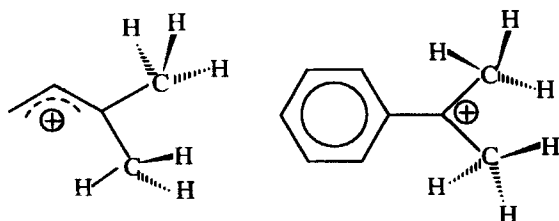
9. Angle type $C(sp^2)-C(sp^3)-H$. The bending parameters for this angle type are treated analogously to angle type $C(sp^2)-C(sp^3)-C(sp^3)$. The variation of the angle constant is given by eq. (44). We used a slight modification of eq. (43) to calculate the new angle parameter.

$$Ang(i, k, l) = 110. - 3030 \cdot F \text{ hyp}^2(i, k, l) \quad (45)$$

Torsional Parameters

We performed a number of *ab initio* calculations on classical cations to find torsional parameters for the correct reproduction of these structures by MMP2. The 1,1-dimethylallyl cation proved to have C_1 symmetry with an almost eclipsed conformation of the endo methyl group and a perpendicular conformation of the exo methyl group. On the other hand, we found a minimum structure of C_2 symmetry for α,α -dimethylbenzyl cation with a dihedral angle of 23.4° of the eclipsed hydrogen

atoms toward the planar π -system.



We did not succeed in finding torsional parameters for dihedral angles of type $C(sp^3)-C(sp^2)-C(sp^3)-H$ that reproduced both structures satisfactorily. We felt that the reasons for this failure are charge-charge repulsions and charge-charge attractions of the different atoms depending on the chemical environment of the individual atoms. Therefore, we decided to replace the torsional constants of a dihedral angle depending on the chemical environment of the atoms involved.

MMP2 first looks for the atoms that are bound to the atoms of a dihedral angle and then decides which torsional constants should be assigned to this angle. Furthermore, we changed the torsional constants of a dihedral angle depending on the charges of the participating $C(sp^2)$ atoms. Table VI lists the torsional constants and the conditions which determine their assignment.

Twofold Torsional Constants for Dihedral Angles Containing Two Central sp^2 Carbons. According to Allinger's method, twofold torsional constants of dihedral angles with two central sp^2 carbons are modified by the bond orders of the central bond:

$$k = V2 \cdot Pbpl(i) \quad (46)$$

where k is the torsional constant to be calculated, $V2$ is the torsional parameter, and $Pbpl(i)$ is the

TABLE VII.
Variation Factors Fact for Twofold Torsional Constants and Conditions that Determine Their Assignment.

Angle Type	Fact	Conditions that Determine Assignments
$C(sp^3)-C(sp^2)-C(sp^2)-C(sp^3)$	2.0	$C(sp^2)$ atoms do not terminate a row of $C(sp^2)$ atoms
	1.0	All other dihedral angles
$C(sp^2)-C(sp^2)-C(sp^2)-C(sp^3)$	0.70	Another $C(sp^3)$ atom is attached to the third $C(sp^2)$ atom
	1.20	All other dihedral angles
$C(sp^2)-C(sp^2)-C(sp^2)-H$	0.80	Second $C(sp^2)$ atom is a tertiary $C(sp^2)$ atom and two hydrogen atoms are attached to the third $C(sp^2)$ atom
	1.30	Second $C(sp^2)$ atom is a tertiary $C(sp^2)$ atom and no other hydrogen atoms are attached to the third $C(sp^2)$ atom
	0.25	The two central $C(sp^2)$ atoms do not carry a positive charge; the third $C(sp^2)$ atom is carrying a positive charge
	0.55	None of the three $C(sp^2)$ atoms is carrying a positive charge
	0.65	All other dihedral angles
$H-C(sp^2)-C(sp^2)-H$	0.75	One of the two central carbon atoms is carrying a positive charge
	1.00	All other dihedral angles
$C(sp^2)-C(sp^2)-C(sp^2)-C(sp^2)$	0.55	Only one of the two terminal $C(sp^2)$ atoms (and no other carbon atom) is carrying a positive charge
	0.20	Only one of the two terminal $C(sp^2)$ atoms is carrying a positive charge and the two central $C(sp^2)$ atoms are tertiary atoms
	0.85	One of the two central $C(sp^2)$ atoms is carrying a positive charge and at least one of the two central atoms is a tertiary $C(sp^2)$ atom
	0.65	One of the two central $C(sp^2)$ atoms is carrying a positive charge
	1.0	All other dihedral angles
$C(sp^3)-C(sp^2)-C(sp^2)-H$	1.50	—

bond order of the central C(sp²)-C(sp²) bond according to SCF calculation for the planar π -system.

We changed eq. (46) by adding a factor depending on the kind of the dihedral angle and the charge of the participating sp² carbons. We assumed a V2 value of 8.0 for all kinds of dihedral angles with central C(sp²) atoms.

$$k = V2 \cdot \text{Pbpl}(i) \cdot \text{fact} \quad (47)$$

Table VII lists the assumed variation factors and the conditions that determine their assignment.

Van Der Waals Parameters

The van der Waals parameters of C(sp²) atoms and C(sp³) atoms, attached to a C(sp²) atom and hydrogen atoms, which are attached to C(sp²) atoms and C(sp³) atoms bound to an sp² atom, are changed depending on the charge of the C(sp²) atom. The van der Waals radii and the hardness parameters are multiplied with a factor depending on the charges of the C(sp²) atoms:

$$r(i) = r(i) \cdot \text{fcor} \quad (48)$$

$$\varepsilon(i) = \varepsilon(i) \cdot \text{fcor} \quad (49)$$

where $r(i)$ is the van der Waals radius of atom i , $\varepsilon(i)$ is the hardness parameter of atom i , and fcor is the correcting factor.

Table VIII lists the developed formulas for the correcting factor and the conditions which determine the assignment of this factor.

PARAMETERIZATION OF HEATS OF FORMATION

Principal Procedure

The experimentally determined heat of formation of the methyl cation is 261.3 kcal/mol.³⁰ With respect to increments for three ⁺C-H bonds in the methyl cation, we deduced an increment for C⁺ of 281.5 kcal/mol.

Localized Cations. The increment for C⁺ in connection with eqs. (14) and (17) produces satisfying results for heats of formation of localized cations. No other increments are necessary.

Delocalized Cations. The allyl cation is described as a methyl cation substituted by one vinyl group. Consistently, we had to remove one "C-C deloc" increment, and only the remaining increment for the vinyl group is necessary. Subsequently, we

TABLE VIII.
Assignment of Correcting Factors fcor for the van der Waals Parameters.

Correcting Factor	Conditions for Assignment of the Correcting Factor
fcor = 1. - 1.16 · Plad ² Plad = 1. - Ed(k, k)	Hydrogen atom attached to a C(sp ²) atom k carries a positive charge
fcor = 1. - 1.5 · Plad Plad = 1. - Ed(k, k)	Hydrogen atom attached to a C(sp ²) atom k with high electron density
fcor = 0.80	Hydrogen atom of a methyl group attached to a C(sp ²) atom carrying a positive charge
fcor = 0.98	All other hydrogen atoms
fcor = 0.95 - 1.52 · Plad Plad = 1. - Ed(i, i);	C(sp ²) atom i with high electron density (larger than 1.0)
fcor = 0.80	C(sp ²) atoms carrying a positive charge
fcor = 0.80	C(sp ³) atoms attached to C(sp ²) atoms carrying a positive charge
fcor = 0.90	C(sp ³) atoms attached to C(sp ²) atoms that do not carry a positive charge

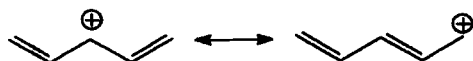
Ed: Density matrix element.

had to look for the "⁺C-C(sp²)" increment. By comparing the SCF σ -energies for the C(sp²) skeleton of ethene and allyl cation, we concluded an increment of 90.0 kcal/mol for "⁺C-C(sp²)". In general, MMP2 looks for the sp² carbon, which is carrying the major part of the positive charge, and computes the number of C(sp²) atoms attached to it. A delocalized cation is considered as a localized system with the charge lying on the carbon atom, presenting minor electron density. The computed number of "C-C deloc" increments is reduced by the number of C(sp²) atoms that are bound to this atom. The same number of "⁺C-C(sp²)" increments is added. The weakness of this method is the fact that, for example, the 1,3-pentadien-5-yl cation can be regarded as a methyl cation substi-

TABLE IX.
Increments for the Calculation of the Heats of Formation of Localized and Delocalized Carbocations.

Name of the Increment	Assumed Value / kcal / mol	Structural Feature
^+C	281.50	All cations
$^+C-C(sp^2)$	90.00	All delocalized cations
sec.-deloc.	0.10	Secondary delocalized cation that can be regarded as primary delocalized cation
tert.-deloc	2.50	Tertiary delocalized cation that can be regarded as primary delocalized cation
sec.-tert. correction	-1.30	Tertiary delocalized cation that can be regarded as secondary delocalized cation
prim.-sec. deloc	-2.49	Primary delocalized cation that can be regarded as secondary delocalized cation
prim.-tert. deloc	-4.54	Primary delocalized cation that can be regarded as tertiary delocalized cation
sec.-tert. deloc	-3.60	Secondary delocalized cation that can be regarded as tertiary delocalized cation

tuted by two vinyl groups, but it can also be regarded as a methyl cation substituted by one butadienyl group. This difficulty could be overcome by adding correction increments. MMP2 looks for other possibilities to describe the delocalized system according to resonance theory. If the program finds a cationic carbon atom that is bound to two other $C(sp^2)$ atoms (e.g., 1,3-pentadien-5-yl cation) but the system can be regarded as a cation with a center that is bound to only one $C(sp^2)$ atom too, the program adds a correction increment for "C-sec-C-prim-deloc". These correction increments are chosen in a way that a shift of charge by alkyl substitution does not lead to a variation of the increments of the $C(sp^2)$ system. Table IX lists the increments for localized and delocalized cations.



Results

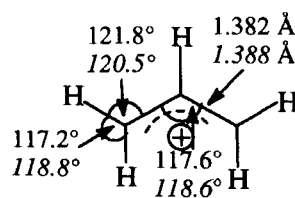
The calculated heats of formation are listed and compared with experimental data in Table X. Table X does not contain protonated aromatic systems

because these systems proved to be treated differently, as will be reported elsewhere.

Examples

ALLYL CATION

The ^{13}C -NMR chemical shift of allyl cations,^{32,33} formed by protonation of alkynes in magic acid solutions,³⁴ was investigated several years ago. The geometry parameters at MMP2 and at MP2(full)/6-31G* are similar. MMP2 reproduces the C-C bond lengths excellently (i.e., Allinger's assumption that bond length parameters depend linearly on the bond orders of the π -system works well). Both methods agree in calculating a slightly reduced $C(sp^2)-C(sp^2)-C(sp^2)$ angle due to the homoconjugation between the terminal allyl carbons.



italic: values at MMP2

TABLE X.
MMP2 and Experimental Heats of Formation of Carbocations.

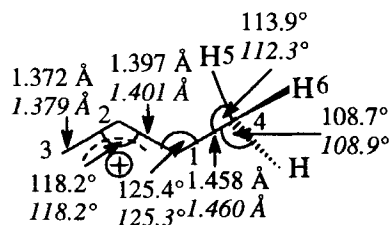
Cation	ΔH_f Determined by Experiment / kcal / mol	ΔH_f Calculated by MMP2 / kcal / mol
Methyl cation	261.4	260.9
Ethyl cation	218.5	222.0
<i>n</i> -Propyl cation	211	212.1
<i>n</i> -Butyl cation	203	202.9
2-Propyl cation	190.9	191.7
2-Butyl cation	183	182.7
<i>i</i> -Butyl cation	199	199.5
<i>t</i> -Butyl cation	165.8	164.9
Cyclopentyl cation	191.4	190.5
<i>n</i> -Pentyl cation	194	194.1
2-Pentyl cation	175	175.0
2-Methyl-2-butyl cation	158	157.5
2,2-Dimethyl- <i>n</i> -propyl cation	190	190.0
<i>n</i> -Hexyl cation	191	188.8
2-Hexyl cation	168	166.6
2-Methyl-2-pentyl cation	152	152.7
2,4-Dimethyl-2-butyl cation	150	149.0
3-Methyl-3-pentyl cation	152	152.2
Cyclohexyl cation	175	176.0
1-Methyl-cyclopentyl cation	167	166.7
2-Methyl-cyclopentyl cation	179	180.0
1-Methyl-cyclohexyl cation	157	154.4
2-Methyl-cyclohexyl cation	169	167.4
3-Methyl-cyclohexyl cation	173	173.0
4-Methyl-cyclohexyl cation	172	171.2
1,2-Dimethyl-cyclopentyl cation	158	159.5
<i>n</i> -Heptyl cation	183	182.8
2-Heptyl cation	162	162.1
2-Methyl-2-hexyl cation	147	145.3
2,4-Dimethyl-2-pentyl cation	148.4	146.4
3-Ethyl-3-pentyl cation	150.6	151.3
2,3,3-Trimethyl-2-butyl cation	144.5	146.4
2-Methyl-2-heptyl cation	139	139.4
4-Methyl-4-octyl cation	133	134.0
Allyl cation	226	225.0
1-Methylallyl cation	202	202.7
2-Methylallyl cation	211	211.0
1,1-Dimethylallyl cation	183	182.5
1,3-Dimethylallyl cation	182	180.7
1,2-Dimethylallyl cation	190	188.4
1-Ethylallyl cation	193	194.5
1,1,3-Trimethylallyl cation	169	167.7
1,2,3-Trimethylallyl cation	170	172.3
1,1,2-Trimethylallyl cation	174	175.2
1,1,3,3-Tetramethylallyl cation	157	156.1
Pentamethylallyl cation	152	153.1
Cyclopenten-3-yl cation	199	198.5
Cyclohexen-3-yl cation	191	189.0
1,3,5,5-tetramethyl-cyclohexen-3-yl cation	148	150.2
Cyclopentadienyl cation	252	252.6
Tropylium cation	203	202.4
Benzyl cation	215	215.4
α -Methylbenzyl cation	199	200.6

TABLE X.
(continued)

Cation	ΔH_f Determined by Experiment / kcal / mol	ΔH_f Calculated by MMP2 / kcal / mol
2-Methylbenzyl cation	203	203.6
3-Methylbenzyl cation	204	203.9
4-Methylbenzyl cation	200	200.7
α -Methyl-4-methylbenzyl cation	186	186.0
α, α -Dimethylbenzyl cation	186	187.2
α, α -Dimethyl-4-methylbenzyl cation	174	176.4
α -Methylbenzhydryl cation	213	213.6
2-Naphthylmethyl cation	229	227.5
1,3-Pentadien-5-yl cation	220	220.1
1-Adamantyl cation	159	158.3
2-Adamantyl cation	168	166.4

^a See ref. 31.**1-METHYLALLYL CATION**

The scheme below shows that the shift of π -electrons in the 1-methylallyl cation³⁵ from C1 to C2 and C3, which induces an elongation of bond C1–C2 and a shortening of bond C2–C3, is described realistically by MMP2 (c.f. electron densities in Table I). The shortening of bond C1–C4 due to hyperconjugation of the methyl group is reproduced by MMP2 correctly. The hyperconjugation of bond C4–H6 leads to a diminution of angle C1–C4–H6 and consequently to an enlargement of angle C1–C4–H5. Both methods compute very similar angles as a result of this effect.

*italic: values at MMP2*

Conformational analysis on the 1-methylallyl cation was studied by *ab initio* methods (STO-3G basis set) several years ago.³⁶ The STO-3G basis set gives only poor and unreliable results, but computations at larger basis sets could not be performed due to a lack of computer time in 1979. We calculated two conformers of the (*E*)-1-methylallyl and (*Z*)-1-methylallyl cations with eclipsed and staggered conformations of one methyl C–H bond toward the planar allyl system at MP4sdtq/6-31G*//MP2(full)/6-31G* and MMP2. Table XI lists the results for the four possible conformers.

TABLE XI.
Relative Energies E_{rel} of 1-Methylallyl Cation Conformers at MP4sdtq / 6-31G* // MP2(full) / 6-31G*, Their MMP2 Relative Heats of Formation $\Delta H_f(\text{rel})$, Number of Imaginary Frequencies (NIMAG), and *Ab Initio* Energies at MP2(full) / 6-31G* // MP2(full) / 6-31G* (EMP2) and MP4sdtq / 6-31G* // MP2(full) / 6-31G* (EMP4).

Conformer	E_{rel} (MP4) / kcal/mol	$\Delta H_f(\text{rel})$ (MMP2) / kcal/mol	NIMAG	EMP2 / a.u.	EMP4 / a.u.
	0.00	0.00	0	-155.75538	-155.80038
	1.18	1.27	1	-155.75351	-155.79850
	3.11	3.62	0	-155.75007	-155.79542
	5.04	4.66	1	-155.74680	-155.79234

The eclipsed conformers are favored over the staggered structures due to a better torsional energy according to MMP2 [(*E*)-isomer: 1.27 kcal/mol, (*Z*)-isomer: 1.04 kcal/mol in favor of the eclipsed conformers]. We looked at the NBO analysis of the different conformers to find the reasons for the preference of the eclipsed conformations over the staggered structures and recognized that a σ - σ^* hyperconjugation effect of the C–H bond parallel to the π -system with the

$C(sp^2)-C(sp^2)-\sigma^*$ orbital is the most probable explanation for the preference of the eclipsed conformers. This electronic effect is the best physical correlative for negative threefold torsional constants of dihedral angles of angle type $C(sp^2)-C(sp^2)-C(sp^3)-H$. The exo conformers are favored over the endo conformers due to better van der Waals energies, bending energies, and torsional energies. The MMP2 SCF energies of the conformers are almost identical. Therefore, the energetic differences of the conformers are mainly caused by steric effects, and hyperconjugation effects play only a minor part.

1,1-DIMETHYLLALLYL CATION

We had great difficulties in reproducing the minimum structure of 1,1-dimethylallyl cation, which has already been examined by Wiberg and co-workers at MP2/6-31G*,³⁵ because of the small distance of hydrogen atoms 9 and 12 (c.f. Fig. 2). The correct parameterization of the van der Waals constants is of great importance for an accurate calculation of this structure by force field methods. Figure 2 lists the important geometric properties, computed by MP2(full)/6-31G* and MMP2 optimizations.

Both methods give comparable results for $C(sp^2)-C(sp^2)$ bond lengths (i.e., the shift of π -electrons from atom 1 to atoms 2 and 3, which induces an elongation of bond C1-C2 and a shortening of bond C2-C3, is reproduced correctly by MMP2). Nevertheless, comparison of the results for bond lengths C1-C4, respectively, C1-C5, and angles C1-C4-H6, respectively, and C1-C5-H10 show a slight underestimation of hyperconjugation by MMP2.

α,α -DIMETHYLBENZYL CATION

The MP2(full)/6-31G* optimization gave C_2 symmetry for the α,α -dimethylbenzyl cation. Figure 2 compares the MP2(full)/6-31G* minimum structure of this cation as well as the minimum structures of the 1,1-dimethylallyl, 3-methyl-3-pentyl, cyclopentyl, and adamantyl cations with those obtained by MMP2 optimizations.

The results show that the elongation of bond C1-C2 due to hyperconjugation effects in comparison with the unsubstituted benzyl cation (MP2(full)/6-31G*: 1.372 Å; MMP2: 1.373 Å) is reproduced correctly by MMP2. The computed angles and dihedral angles are in good agreement. The deviation of this cation from C_{2v} symmetry is

reproduced by MMP2 correctly not only as far as geometry is concerned by also as far as energy is concerned (the C_2 structure is favored by 0.77 kcal/mol according to MMP2; the energy difference at MP4sdq/6-31G*//MP2(full)/6-31G* is 0.66 kcal/mol). Table XII lists *ab initio* energies for these structures and other cations discussed in this article.

3-METHYL-3-PENTYL CATION

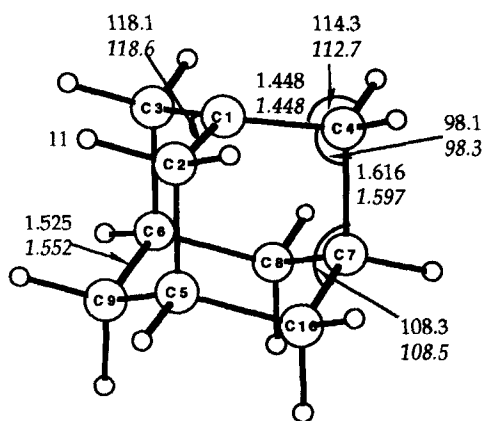
The 3-methyl-3-pentyl cation is presented as a typical example for a localized classical carbocation with strong hyperconjugation effects. Figure 2 lists the structural features, which show these hyperconjugation effects computed by MP2(full)/6-31G* and MMP2 optimizations. MMP2 describes the C-C hyperconjugation and C-H hyperconjugation effects realistically. The bond lengths of $C(sp^2)-C(sp^3)$ bonds and $C(sp^3)-C(sp^3)$ bonds are calculated very close to the *ab initio* results. MMP2 tends toward a slight overemphasis of the attempt of strong hyperconjugating bonds to move perpendicular to the plane of the cationic $C(sp^2)$ atom.

CYCLOPENTYL CATION

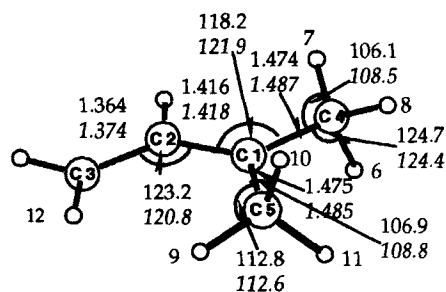
Early *ab initio* calculations of Koch and Schleyer³⁷ showed that the classical cyclopentyl cation is a chiral molecule with C_2 symmetry, which is reproduced by MMP2. Figure 2 lists interesting geometric properties of this structure at MP2(full)/6-31G* and MMP2. The results show that *ab initio* methods tend to favor one very strong hyperconjugation interaction over two intermediate hyperconjugation interactions, in contrast to MMP2. MMP2 compensates for the weaker hyperconjugative effect of bond C2-H6 by a stronger hyperconjugation of bond C2-H7. This fault of MMP2 has been found for more examples, with the cationic center as a part of a five-membered ring, and may be a result of the problems of MMP2 with five-membered rings in general.

1-ADAMANTYL CATION

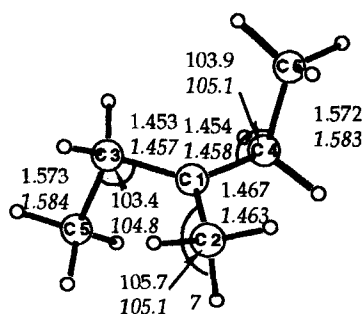
Figure 2 lists the result for the adamantyl cation, which has already been examined by X-ray techniques,¹¹ with its strong hyperconjugation interactions at MP2(full)/6-31G* and MMP2. The large hyperconjugation effect of the three $C(sp^3)-C(sp^3)$ bonds, which leads to an elongation of bond C2-C5, to a shortening of bond C1-C2, to a decrease of angle C1-C2-C5, and consequently, to a



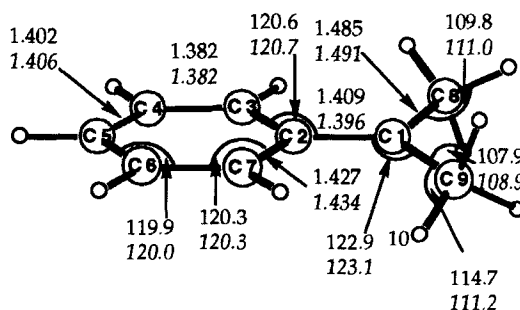
Out of plane angle C1: 8.1
6.9



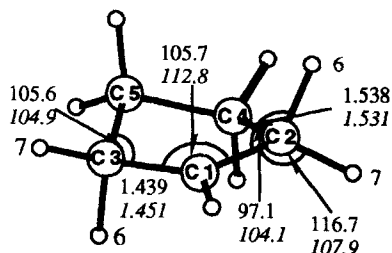
Dihedral angles:
C1-C1-C5-H9 12.6
C1-C1-C5-H10 11.5
C2-C1-C5-H10 -108.7
C2-C1-C5-H11 -109.2
C2-C1-C4-H6 -90.0
C2-C1-C4-H7 -98.1
C2-C1-C4-H8 27.1
C2-C1-C4-H9 22.2



Dihedral angles:
C2-C1-C3-C5 92.2
C2-C1-C3-C6 88.4
C2-C1-C4-C6 79.8
C2-C1-C4-C7 88.4
C3-C1-C2-H7 79.9
C3-C1-C2-H8 86.4



Dihedral angle:
C2-C1-C9-H10 23.4
C2-C1-C9-H11 23.2



Dihedral angles:
C2-C1-C3-H7 101.2
C2-C1-C3-H8 113.0
C2-C1-C3-H9 -148.4
C2-C1-C3-H10 -135.6
C2-C1-C3-C5 -10.9
C2-C1-C3-C6 -9.1

a. Bond lengths in Å, angles and dihedral angles in degrees. b. Calculations by W. Koch
c. *Italic*: Values at MMP2.

FIGURE 2. Geometry parameters^a of the 1-adamantyl, 1,1-dimethylallyl, 3-methyl-3-pentyl, α,α -dimethylbenzyl, and cyclopentyl^b cations at MP2(full) / 6-31G* and MMP2^c.

TABLE XII.
***Ab Initio* Energy of Cations at MP2(full) / 6-31G* //**
MP2(full) / 6-31G* (EMP2) and MP4 / 6-31G* //
MP2(full) / 6-31G* (EMP4)^a.

Cation	EMP2 / au	EMP4 / au
Allyl cation	-116.55763	-116.59211
1,1-Dimethylallyl cation	-194.94323	-194.99904
α, α -Dimethylbenzyl cation C_2	-384.14973	-384.16895
α, α -Dimethylbenzyl cation C_{2v}	-384.14863	-384.17000
3-Methyl-3-pentyl cation	-235.30950	-235.37994
Cyclopentyl cation ^b	-194.93824	-194.99150
1-Adamantyl cation	-388.51759	-388.55250

^aThe MP4dstq/6-31G* // MP2(full) / 6-31G* level is employed for the allyl, 1,1-dimethylallyl, 3-methyl-3-pentyl, and cyclopentyl cations; the other data are calculated at MP4sdq / 6-31G* // MP2(full) / 6-31G*.

^bCalculations by W. Koch.

slight spread of angle C1-C2-H11, is reproduced by MMP2 correctly. The small out-of-plane angles of the cationic center, which we believe to be a consequence of an optimal σ - π^* overlap, confirm the enlargement of the out-of-plane bending constants according to eq. (32).

Conformational Analysis

Some examples will be presented to show that MMP2 calculations on cations lead to reasonable results.

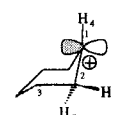
CYCLOHEXYL CATION

Unpublished calculations³⁷ have shown that the cyclohexyl cation is a very interesting system, because different conformers have different contributions of C-C and C-H hyperconjugation effects. Three conformers, which proved to be minima at HF/6-31G*, are of main interest. Two conformers with C_2 and C_s symmetry present very strong C-H hyperconjugation effects and negligible C-C hyperconjugation effects. One conformer with C_s symmetry presents very strong C-C hyperconjugation (c.f. Table XIII). MMP2 reproduces the minimum structures well. Table XIII shows the calculated energies at MP4sdq/6-31G* // MP2(full) / 6-31G* and the MMP2 relative heats of formation.

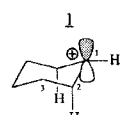
The *ab initio* energies are reproduced by MMP2 well, and only the C_2 conformer is found to be slightly to stable. Interesting features of the computed geometries showing the different hypercon-

TABLE XIII.
Interesting Geometric Parameters of Cyclohexyl
Cation Conformers, Relative Energies E_{rel} of these
Conformers at MP4sdq / 6-31G* // MP2(full) / 6-31G*,
MMP2 Relative Heats of Formation $\Delta H_f(rel)$,
and *Ab Initio* Energies^a at MP2(full) / 6-31G* //
MP2(full) / 6-31G* (EMP2) and MP4sdq / 6-31G* //
MP2(full) / 6-31G* (EMP4).

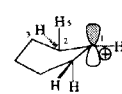
Geometric feature	MP2(full)/6-31G*	MMP2
Conformer 1		
Bonds		
C1-C2	1.428 Å	1.434 Å
C2-C3	1.627 Å	1.588 Å
Dihedral angles		
H4-C1-C2-C3	88.3°	98.2°
H4-C1-C2-H5	-25.6°	-20.1°
Conformer 2		
Bonds		
C1-C2	1.441 Å	1.448 Å
C2-C3	1.530 Å	1.525 Å
Dihedral angles		
H4-C1-C2-C3	-170.6°	-177.1°
H4-C1-C2-H5	-69.9°	-57.9°
Conformer 3		
Bonds		
C1-C2	1.441 Å	1.443 Å
C2-C3	1.531 Å	1.530 Å
Dihedral angles		
H4-C1-C2-C3	-154.3°	-160.2°
H4-C1-C2-H5	89.6°	81.4°



C_s hyperconjugating
C-C bonds



C_s hyperconjugating
C-H bonds



C_2 hyperconjugating
C-H bonds

	E_{rel} / kcal/mol	$\Delta H_f(rel)$ / kcal/mol	EMP2 / a.u.	EMP4 / a.u.
Conformer 1	0.00	0.0	-234.12421	-234.15865
Conformer 2	2.06	3.5	-234.11693	-234.15536
Conformer 3	5.58	4.1	-234.11152	-234.14975

^a Calculations by W. Koch.

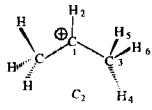
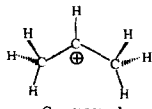
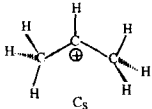
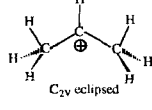
jugation effects clearly are listed in Table XIII.

The geometries confirm the outstanding strong C-C hyperconjugation of conformer 1 and the negligible contribution of this interaction in the conformers 2 and 3. The presented dihedral angles prove a strong C-H hyperconjugation in conformer 2 and especially in conformer 3. MMP2 tends toward a slight diminishing of the dominating hyperconjugative effect in favor of weaker effects. Nevertheless, the stability of 1 is according to the MMP2 calculations exclusively caused by a larger hyperconjugative stabilization energy (energetic favor by hyperconjugation: 1 versus 2: 6.96 kcal/mol; energetic favor of 1 versus 3: 5.74 kcal/mol). Conformer 2 has a weaker hyperconjugative effect than 3, but it is favored by steric energy.

2-PROPYL CATION

Ab initio calculations of Schleyer and Koch²⁷ have shown that the 2-propyl cation is a chiral

TABLE XIV.
Relative Energy E_{rel} of 2-Propyl Cation Conformers at MP4sdtq/6-31G*//MP2(full)/6-31G*, MMP2 Relative Heats of Formation $\Delta H_f(\text{rel})$, and Interesting Geometric Parameters of the C_2 Conformer at MP2(full)/6-31G* and MMP2.

Conformer	E_{rel} kcal/mol	$\Delta H_f(\text{rel})$ kcal/mol	Structural feature	MP2(full)/6-31G*
 C_2	0.00	0.00	Bond	
			C1-C3	1.445 Å
			Angles	
			H2-C1-C3	120.2°
 C_{2v} staggered	0.25	0.30	Dihedral angles	
			H2-C1-C3-H4	74.2°
			H2-C1-C3-H5	-42.8°
			H2-C1-C3-H6	-166.5°
 C_s	1.08	0.51		
 C_{2v} eclipsed	3.19	1.40		

molecule with C_2 symmetry. MMP2 confirms these results. The energies of the different possible conformers at MP4sdtq/6-31G*//MP2(full)/6-31G* and their relative heats of formation computed by MMP2 are listed in Table XIV.

The results show that the structure, which was calculated to be most stable by *ab initio* methods, is recognized as an absolute minimum of the energy surface by MMP2, too. Both methods correspond in calculating low rotational barriers and in calculating the same energetic sequence of the different structures. MMP2 recognizes all calculated conformers as minima, while the *ab initio* methods find only the C_2 structure to be a minimum on the energetic hypersurface. Table XIV compares the geometry of the C_2 structure, calculated by the two different methods. MMP2 favors the C_2 structure by steric energy and by hyperconjugation energy.

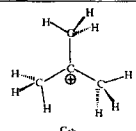
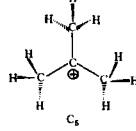
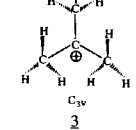
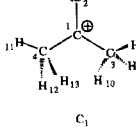
t-BUTYL CATION

Sieber, Buzek, and Schleyer examined four structures of the classical *t*-butyl cation by MP2(full)/6-31G* optimizations.²⁸ This cation has already been examined by X-ray measurements,

but the hydrogen atoms could not be located by these measurements¹²; therefore, the conformation of the *t*-butyl cation could not be detected by experimental methods. We recalculated four chemical structures by MMP2 and found good correspondence of the results, although the energetic sequence of the four conformers calculated by the two different methods are not identical. But this fault of MMP2 seems not to be serious to us because of the low energetic difference of the four conformers. Table XV lists the energies for the different conformers at MP4sdtq/6-31G*//MP2(full)/6-31G* and MMP2. Both methods give low rotational barriers. The C_s conformer is calculated to be to unstable by MMP2. The C_1 structure is favored by MMP2 due to a slightly better hyperconjugation energy.

The geometries are reproduced well by MMP2. Table XV lists interesting geometric properties of

TABLE XV.
Relative Energies E_{rel} of Different Conformers of the *t*-Butyl Cation at MP4sdtq/6-31G*//MP2(full)/6-31G*, Their MMP2 Relative Heats of Formation $\Delta H_f(\text{rel})$, and Interesting Geometric Parameters of the C_1 Conformer at MP2(full)/6-31G* and MMP2.

Conformer	E_{rel} kcal/mol	$\Delta H_f(\text{rel})$ kcal/mol	Structural feature of the C_1 conformer	MP2(full)/6-31G*	MMP2
 C_{3h}	0.04	-0.22	Bonds		
			C1-C2	1.458 Å	1.464 Å
			C1-C3	1.460 Å	1.464 Å
			C1-C4	1.459 Å	1.464 Å
 C_s	0.00	0.00	Dihedral angles		
			C2-C1-C3-H8	80.9°	87.8°
			C2-C1-C3-H9	-161.8°	-153.8°
			C2-C1-C3-H10	-33.2°	-30.1°
			C2-C1-C4-H11	19.4°	20.0°
			C2-C1-C4-H12	148.9°	143.6°
			C2-C1-C4-H13	-96.3°	-98.7°
			C3-C2-C1-H5	-150.1°	-147.0°
			C3-C2-C1-H6	-20.0°	-23.3°
			C3-C2-C1-H7	95.9°	95.3°
 C_{3v}	1.23	0.77			
 C_1	0.00	-0.46			

conformer **4** computed by MP2(full)/6-31G* and MMP2 optimizations.

Conclusions

We have developed a force field method that is able to reproduce geometries of carbocations correctly. Therefore, our work referred to MP2(full)/6-31G* optimizations and the parameters of our force field have been developed according to the geometries obtained by these optimizations. If new X-ray structures of carbocations or calculations on more sophisticated *ab initio* levels lead to new results for these geometries, some of our parameters will have to be replaced. However, our principal procedure of changing parameters according to calculated π -electron densities and according to the chemical environment of atoms should be valid, even if a reparameterization of single parameters becomes necessary. The geometries of cations calculated so far are reproduced with great accuracy. The changes in geometries, which are consequences of hyperconjugation effects, have been the subject of our main efforts in doing a parameterization of cations. Our method is applicable to a wide range of cations. Parameterizations have until now been limited to calculations on tertiary localized cations. Our method enlarges the range of molecules that can be calculated to primary localized and secondary classical cations and all kinds of delocalized classical cations. By the calculation of reasonable SCF energies, the method is able to predict resonance energies and electronic stabilization effects of unsaturated substituents.³⁸ These predictions are completed by homoconjugation effects in delocalized cationic systems.

The complex geometries of carbocations, which may be a consequence of homoconjugation interactions and charge-charge interactions, are reproduced by a parameterization of van der Waals and torsional constants. We found it not to be necessary to introduce charge-charge interactions to MMP2. The exchange of torsional parameters depending on the chemical environment of the participating carbons and on the charges of the C(sp²) atoms is a method that allows a satisfying simulation of these effects.

A second priority of our parameterization has been the calculation of heats of formation. By the correct reproduction of experimental heats of formation, we are encouraged to believe that only

minor reparameterizations will be necessary for calculations on more sophisticated *ab initio* levels. The variation of angles for angle type C(sp²)-C(sp³)-C(sp²) according to the homoconjugation effect of the two marginal carbons may differ for structures calculated on more sophisticated *ab initio* levels.

By the realistic calculation of structures and heats of formation, it is not necessary to parameterize for strain energies. This is the main difference of the method presented in this article from earlier attempts of developing force fields for carbocations. All these force field methods concentrated on the correct calculations of strain energies, since nearly no realistic data for geometries of carbocations have been available. The increasing number of *ab initio* geometries of cations calculated at sophisticated levels allow a parameterization which is not based on strain energies.

Three- and four-membered rings need special parameter sets in MMP2. Parameters for such cationic ring systems have not been developed so far.

Although all structures presented in this article refer to carbocations which could be optimized by correlated *ab initio* methods within a reasonable amount of computer time, the main advantage of this new developed force field method is the possibility of optimizing large cation structures, especially with a large number of C(sp²) atoms. Results for large cationic systems are soon to be published.³⁹

Acknowledgments

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